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Click synthesis of donor–acceptor-type aromatic polymers*

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Abstract: A high-yielding addition reaction between electron-rich alkynes and a small acceptor molecule, tetracyanoethylene (TCNE), was employed as a new click reaction to construct donor–acceptor chromophores in the polymer main chains and side chains. The donor–acceptor alternating conjugated polymers were prepared from the ferrocene-containing poly(aryleneethynylene)s in one step and atom-economic fashion. The energy levels and thermal properties of the aromatic polyamines substituted by electron-rich alkynes as a side chain can be tunable by the amount of the added TCNE. The resulting donor–acceptor-type polymers feature broad charge-transfer (CT) bands in the visible region, potent redox activities, and improved thermal properties.

Keywords: alkynes; charge transfer; click chemistry; conjugated polymers; cycloaddition; electrochemistry; thermal properties.

INTRODUCTION

Post-functionalization is one of the most important techniques to improve polymer properties [1]. The concept of click chemistry, proposed in 2001 by Kolb, Finn, and Sharpless, is based on quantitative conversion under mild conditions, which fits very well with this technique [2]. They raised a renewed interest in the old reaction of the Huisgen 1,3-dipolar cycloaddition between alkynes and azides to yield 1,2,3-triazoles [3] by introducing Cu(I) catalysts, and there have already been many successful examples of the post-functionalization of polymers and materials using this click chemistry [4–8]. Although this reaction is very useful in most cases, there is a limitation regarding the application to conjugated polymers due to the poor optoelectronic properties of the triazole products [9].

We recently started a new project on the post-functionalization of conjugated polymers, directed toward the organic electronic device applications, and therefore sought another suitable click reaction. Fortunately, it was recently found that the electron-rich alkynes activated by suitable electron-donating groups (EDGs) undergo a [2 + 2] cycloaddition with a strong acceptor, tetracyanoethylene (TCNE), to form the cyclobutene rings, which spontaneously open to afford the donor-substituted 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) chromophores in quantitative yields at room temperature (Fig. 1) [10,11]. The reaction had initially been investigated for metal acetylides in 1980s [12], but the reactivity with respect to different donor groups has never been systematically studied [13–15]. Therefore, the finding of suitable donor groups for the quantitative reaction suggests the utility of this

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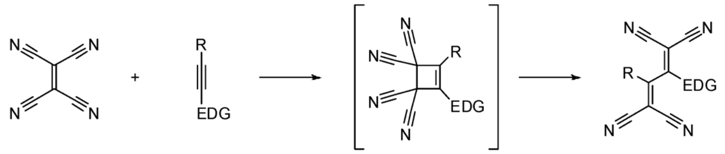

Fig. 1 Reaction mechanism of the click reaction between TCNE and alkynes activated by an EDG to afford donor-substituted TCBDs.

reaction, which actually satisfies most of the requirements of click chemistry as suggested in the original review [2]. The additional important advantages of this reaction over the conventional azide-alkyne click reaction are that no metal catalysts are necessary and the products feature strong charge-transfer (CT) bands in the visible absorption region, potent redox activities in both the cathodic and anodic directions, and related properties, e.g., excellent nonlinear optical effects [16,17]. The currently available donor groups for almost quantitative yields include aromatic amines [18–21], ferrocene [22,23], and azulene derivatives [24,25]. Diederich and others are now extensively expanding this chemistry by applying it to other acceptor molecules, such as 7,7,8,8-tetracyanoquinodimethane (TCNQ) and the derivatives [26–29] as well as the dicyanovinyl and tricyanovinyl derivatives [30,31]. They also succeeded in the syntheses of dendritic donor–acceptor molecules [32], the linear donor–acceptor oligomers by the sequential addition of TCNE and tetrathiafulvalene (TTF) to polyynes [33], and chiral induction in the TCBD moieties [34–36]. However, the application to linear conjugated polymers has remained unexplored. In this paper, we describe our recent results on the click modification of aromatic polymers containing electron-rich alkynes with TCNE. Interestingly, considering the p-type doping ability of TCNE ($E_{\mathrm{red},1}$ = –0.27 V vs. Fc^+/Fc) [37], the procedure is completely the same as the conventional doping of conducting polymers [38]. Although high conductivities are not expected, the resulting polymers are attractive materials for the next generation of organic electronic devices.

REACTIONS IN THE MAIN-CHAIN ALKYNES OF CONJUGATED POLYMERS

The conjugated polymers containing alkyne groups in the main chain can be readily synthesized by the Sonogashira cross-coupling reaction or acetylenic oxidative coupling reaction of diethynylarene derivatives [39]. The resulting poly(aryleneethynylene)s and poly(arylenebutadiynylene)s are an important class of conjugated polymers with fascinating optical and electrical properties [40,41]. In particular, ferrocene-containing poly(aryleneethynylene)s have been well studied [42,43], and the TCNE or TCNQ addition to ethynylferrocene derivatives has also been examined [22,23].

Before starting the polymer project, the model monomer was synthesized and its reactivity toward TCNE was tested [44] (Fig. 2). 1,1'-Bis(phenylethynyl)ferrocene **1**, prepared from 1,1'-diiodoferrocene and phenylacetylene under Sonogashira cross-coupling conditions, was subjected to the reaction with 1 equiv of TCNE, which quantitatively proceeded at 20 °C to yield the donor–acceptor molecule **2**. The further addition of TCNE, however, did not provide the double adduct **3** even upon heating, because of the decreased electron-donating power of the ferrocene substituted by the TCBD acceptor. This result suggests that the ferrocene donor can activate only one alkyne moiety for the TCNE addition.

Single crystals of **2** were analyzed by X-ray crystallography and showed distinctive structural characteristics (Fig. 2). As reported for the other TCBD derivatives [10,11,27,34], significant twisting of the two dicyanovinyl subunits was observed in the TCBD moiety. Thus, the torsion angle θ[C(1)-C(2)-C(3)-C(4)] is –122.8(5)°, which is comparable to that reported previously [22]. Despite the nonplanarity of the TCBD moiety, **2** shows efficient CT interactions between the ferrocene donor and TCBD acceptor. Bond lengths of the cyclopentadienyl ring substituted by the TCBD moiety clearly revealed the fulvene-type resonance contribution. The bond lengths of C(16)–C(17) [1.413(4) Å] and

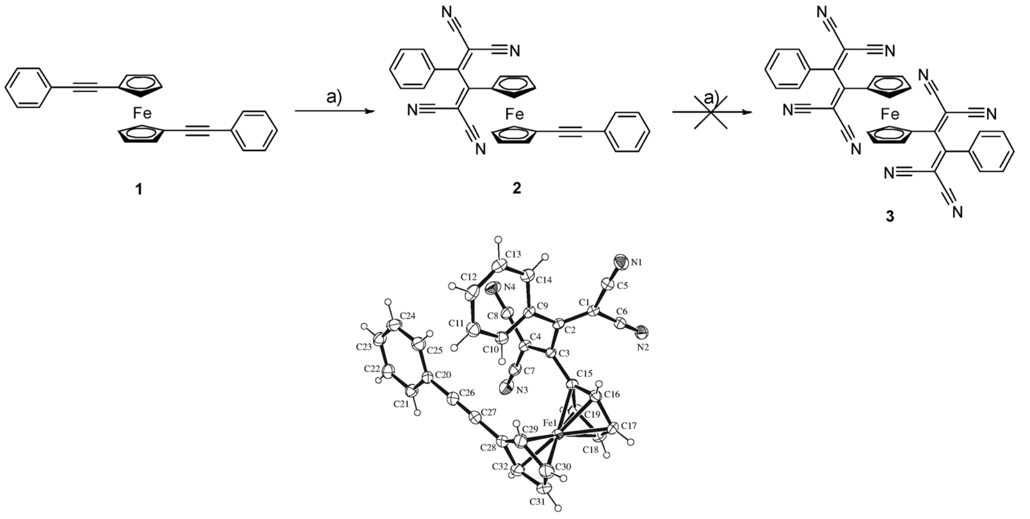

Fig. 2 Addition reaction of TCNE to the alkynes activated by ferrocene monomer and the ORTEP plot of ferrocene-substituted TCBD derivative **2**. (a) TCNE, CH_2Cl_2, 20 °C.

C(18)–C(19) [1.412(4) Å] are much shorter than those of C(15)–C(16) (1.445(4) Å) and C(15)–C(19) [1.441(4) Å]. The bond length of C(3)–C(15) [1448(4) Å] is close to the latter values.

Based on the monomer results, the TCNE click reaction was applied to the ferrocene-containing poly(aryleneethynylene)s (Fig. 3). The precursor polymers **4** and **6** were prepared by the Sonogashira polycondensation between 1,1'-diiodoferrocene and the diethynylbenzene derivatives. The molecular weights of **4** (M_w = 41 100, M_n = 8100) and **6** (M_w = 16 200, M_n = 7000) are sufficiently high. However, in sharp contrast to the high reactivity of **1**, both **4** and **6** did not react with TCNE at room temperature. Slow heating changed the solution color from orange to green, indicating the progress of the TCNE addition. The reaction conditions were carefully optimized on the basis of the thermogravimetric

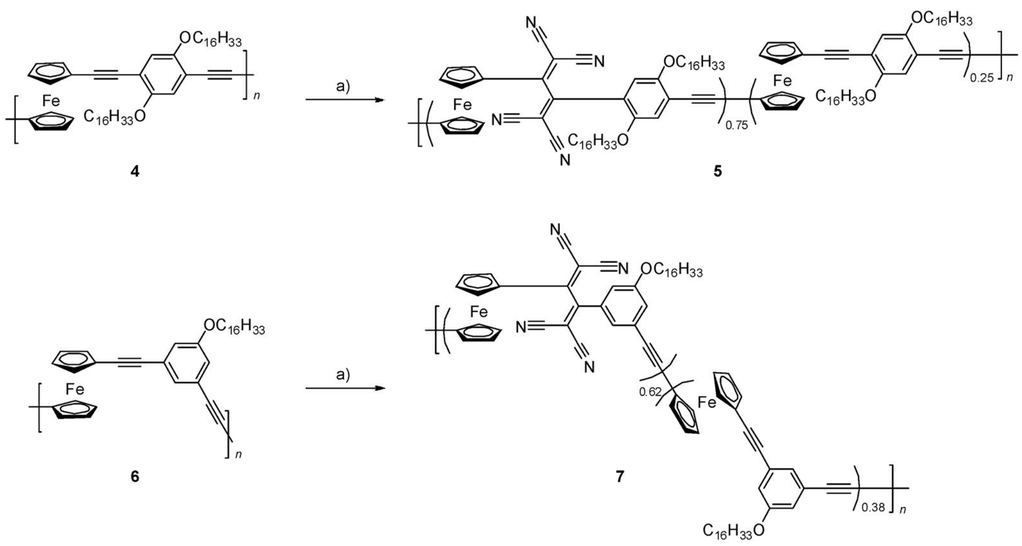

Fig. 3 TCNE click reaction to the main chain alkynes of ferrocene-containing poly(aryleneethynylene)s. (a) TCNE, 1,2-dichlorobenzene, 120 °C, 3 h.

analysis (TGA), and the TCNE addition finally amounted to 0.75 for **5** and 0.62 for **7**. Judging from the NMR and IR spectra, the excess of TCNE did not produce any undesired side reactions and could readily be removed by sublimation or reprecipitation. Therefore, the reaction yields or the amount of the added TCNE can simply be determined by the gravimetric analysis.

In addition to the X-ray crystal structure analysis of **2**, efficient CT interactions were also confirmed by the UV–vis absorption spectra (Fig. 4). The precursor monomer **1** displayed the π–π* transition at 307 nm and d-d transition at 453 nm. The *m*-phenylene-linked polymer **6** showed a peak profile similar to **1**, whereas the π–π* transition of the *p*-phenylene-linked polymer **4** bathochromically shifted to 433 nm, reflecting the longer effective conjugation length. This trend was retained after the TCNE addition. A new CT band appeared at 618 nm for **2** and 603 nm for **7**, whereas **5** showed a very broad CT band without a well-defined peak top. The broad and relatively weak CT bands of the polymers, as compared to the monomer, are probably derived from the incomplete TCNE addition. The end absorption of the TCNE adducts reached ca. 850 nm in the near-IR region, suggesting the corresponding optical bandgap of ca. 1.46 eV. The electrochemical bandgaps, determined by the first oxidation potential ($E_{1,\mathrm{ox}}$) of the ferrocene moiety and the first reduction potential ($E_{1,\mathrm{red}}$) of the TCBD moiety in CH_2Cl_2 with 0.1 M *n*-Bu_4NClO_4, are in the range of 1.16–1.46 V, almost consistent with the optical bandgaps. All the TCNE adducts showed the first reduction at almost the same potential of ca. –0.9 V (vs, Fc^+/Fc) and the TCBD-centered two-reduction steps with perfect reversibility for **2** and quasi-reversibility for **5** and **7**. All these results suggest that electronic communication is almost localized in the repeat unit of the polymers.

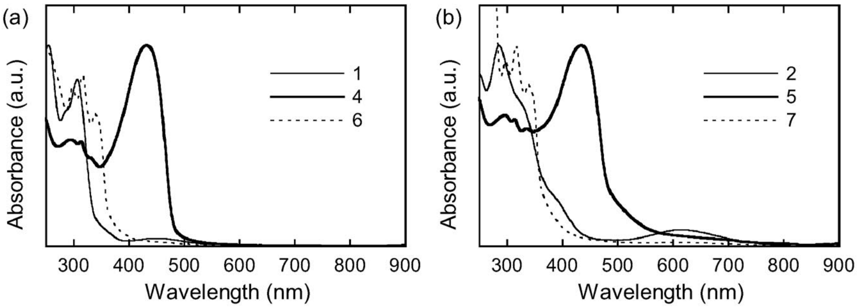

Fig. 4 UV–vis spectra of (a) the ethynylferrocene monomer and polymers and (b) the ferrocene-TCBD monomer and polymers in $CHCl_3$ at 20 °C.

REACTIONS IN THE SIDE-CHAIN ALKYNES OF AROMATIC POLYMERS

In order to elucidate the structure–reactivity relationship of the electron-rich alkynes in the polymers, we designed a new precursor polymer, an aromatic polyamine substituted by the electron-rich alkynes as a side chain. The aromatic amine group was, at the same time, employed as another powerful donor group for the quantitative TCNE click reaction.

The precursor polyamine was prepared by the palladium-catalyzed amination reaction between **8** and the dibromofluorene derivative [45] (Fig. 5). The resulting polymer **10** was characterized by ^{1}H- and ^{13}C-NMR, IR, and gel permeation chromatography (GPC), and the sufficiently high molecular weight (M_w = 45 600, M_n = 13 300) as well as the presence of the alkyne groups were confirmed. As revealed for many dialkylanilino-substituted alkynes, the monomer **8** was quantitatively converted by the reaction with TCNE into the corresponding TCBD product **9** at 20 °C. Similarly, the TCNE addition reaction of the polyamine **10** smoothly proceeded in chlorinated solvents to yield the red-colored donor –acceptor-type polymers. The quantitative addition, demonstrated by the expected peak profile of the matrix-assisted laser desorption/ionization with time-of-flight (MALDI-TOF) mass spectra as well as the absence of the acetylene peak signals in the ^{13}C NMR spectrum (Fig. 6), made it possible to prepare the copolymers bearing the desired TCBD amount (x) without any purification process. Thus, the polymers **11–15** with the different x values at 0.2 intervals were prepared and their electronic and thermal properties were comprehensively studied. Although the polymer solubility dramatically decreased with the increasing TCBD amount, chlorinated solvents showed the satisfactory solubility even for the full adduct **15**. In the UV–vis spectra, the intensity of the original absorption at 402 nm of **10** gradually decreased with the increasing x value (Fig. 7). On the contrary, a new CT band with the

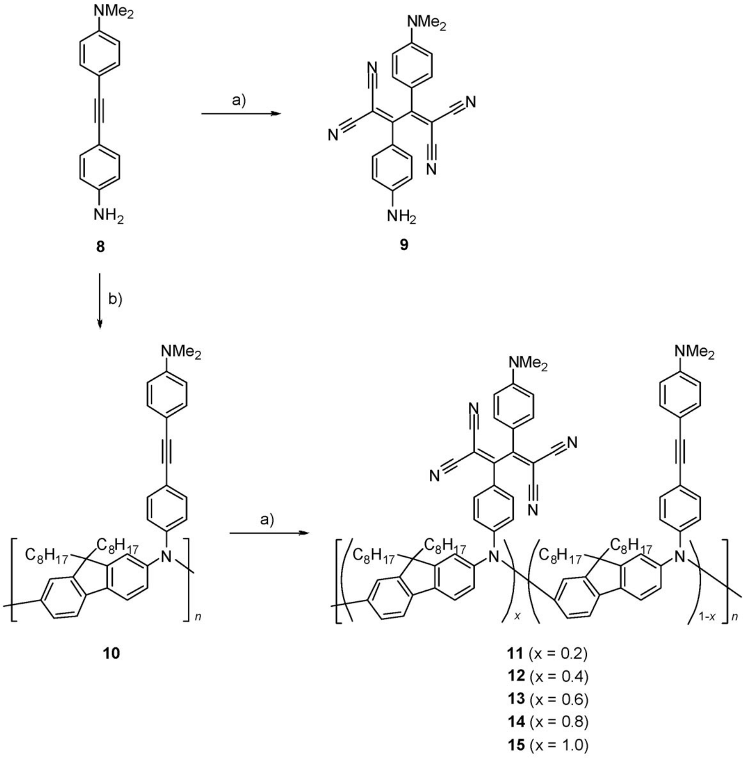

Fig. 5 Synthesis of aromatic polyamine and the TCNE click reaction to the alkynes activated by the aromatic amine groups. (a) TCNE, CH_2Cl_2 or 1,2-dichloroethane, 20 °C; (b) 9,9-dioctyl-2,7-dibromofluorene, $Pd_2(dba)_3$, P(t-Bu)$_3$, NaOt-Bu, toluene, 60 °C, 24 h.

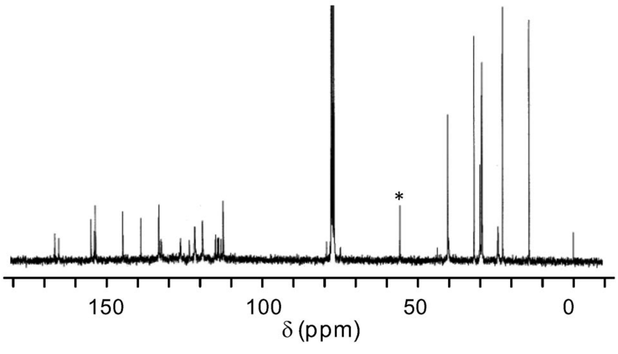

Fig. 6 ^{13}C NMR spectrum of **15** (x = 1.0) in $CDCl_3$ at 20 °C. The residual CH_2Cl_2 peak was marked.

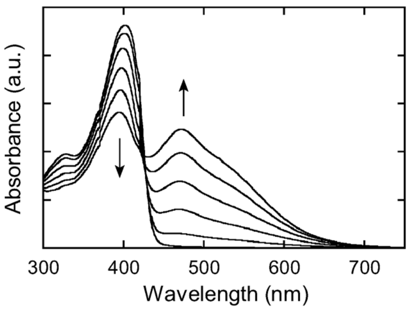

Fig. 7 UV–vis spectra of **10** (x = 0), **11** (x = 0.2), **12** (x = 0.4), **13** (x = 0.6), **14** (x = 0.8), and **15** (x = 1.0) in 1,2-dichloroethane at 20 °C. The arrows represent the increase in the TCNE addition amount.

most intense absorption centered at ca. 470 nm appeared, but the intensity gradually increased. The presence of the isosbestic point at 428 nm indicates there is no side reaction during this click reaction. The broad CT absorption with the peak top and several shoulders suggests the presence of multiple donor–acceptor interactions with different strengths, which thereby covers the entire visible range. The end absorptions of **11–15** reached ca. 780 nm, corresponding to the optical bandgap of ca. 1.6 eV. The optical bandgaps were almost similar to the electrochemical bandgaps.

Further extensive studies revealed that the TCNE click reaction to the polymer side chains can control the energy levels of the aromatic polyamine and simultaneously improve the thermal properties. For example, the peak top values of the CT absorption bathochromically shifted with the increasing amount of the TCNE addition, indicating the electronic interactions between side-chain chromophores through the aromatic polymer main chain (Table 1). The possibility of the through-space interaction induced by the chromophore aggregation was ruled out by the titration experiment of the model monomer **10** with TCNE. Moreover, the $E_{\mathrm{red},1}$ values of **11–15**, determined by differential pulse voltammetry (DPV), linearly shifted in the anodic direction with the increasing TCNE addition amount. The $E_{\mathrm{ox},1}$ and $E_{\mathrm{red},1}$ values qualitatively represent the electronic highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, respectively. Thus, the TCNE addition efficiently lowers the LUMO levels or increases the electron-accepting character of the aromatic polyamine. Note that the precursor polyamine **10** was a typical p-type semiconductor with the HOMO level of –4.9 eV and LUMO level of –2.1 eV. However, the energy level of the fully TCBD adducted polymer **15** (HOMO: –5.8 eV, LUMO: –4.2 eV) was rather close to that of an n-type semiconductor, e.g., [6,6]-phenyl-C61-butyric acid methyl ester (PCBM; HOMO: –6.0 eV, LUMO: –4.2 eV) [46].

Table 1 Changes in electronic and thermal properties of aromatic polyamine upon TCNE addition.

Polymer	x	$\lambda_{\max}$ (nm)[a]	$E_{\mathrm{red},1}$ (V)[b]	T_g (°C)[c]	T_d (°C)[d]
10	0	–	–	125	291
11	0.2	466.5	–0.696	129	368
12	0.4	468.5	–0.676	141	381
13	0.6	470.0	–0.668	146	387
14	0.8	471.5	–0.612	149	400
15	1.0	472.0	–0.608	152	409

[a] Measured in 1,2-dichloroethane at 20 °C.
[b] Determined by DPV in CH_2Cl_2 with 0.1 M n-Bu_4NClO_4.
[c] Glass transition temperature determined by DSC measurements.
[d] Decomposition temperature determined by derivative thermogravimetry.

Another important feature of this click chemistry to provide products for material applications is the improvement of thermal properties. Both the glass transition temperature (T_g) and decomposition temperature (T_d) of the polyamines, determined by differential scanning calorimetry (DSC) and TGA, respectively, apparently increased with the increase in the TCNE addition (Table 1). The temperature increase from **10** to **15** amounted to 27 °C for the T_g values and 118 °C for the T_d values. These enhancements most likely originate from the strong dipolar- or multipolar-type interactions between the electronically stabilized cyano groups, which were partially demonstrated from the X-ray crystal structures of the small TCBD molecules [11,26,27,29].

CONCLUSION

Synthetic routes to donor–acceptor-type aromatic polymers using the TCNE click reaction were established. Previous syntheses of donor–acceptor alternating conjugated polymers have mainly relied on the metal-catalyzed polycondensations between the donor monomer and acceptor counter monomer. The one-step, atom-economic transformation from readily accessible poly(aryleneethynylene)s is a completely new methodology. This click chemistry is expected to spread over a wide variety of alkyne-containing conjugated molecules and polymers in combination with different acceptor molecules. For example, the addition products of TCNQ analogs show bathochromically shifted absorptions and narrower bandgaps when compared to the corresponding TCNE adducts [26]. Therefore, the polymer energy levels would be more finely controlled in response to the requirements of the intended devices by the amount and the species of acceptors added to the side-chain alkynes.

The obtained donor–acceptor-type polymers are ready for the next stage. The small donor-substituted TCBD molecules can be sublimed without decomposition in order to prepare homogeneous and amorphous thin films [16,17]. In the case of polymers, thin films can be prepared by low-cost methods, such as spin- and spray-coating techniques. Furthermore, the polymer thin films ensure a high purity because of the metal-free post-functionalization. Since a small amount of metal impurities is supposed to significantly decrease the device performance, this click chemistry will become a valuable post-functionalization technique of conjugated polymers used for organic optoelectronic devices, such as nonlinear optics and photovoltaics.

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